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WO₃–SiO₂ nanomaterials synthesized using a novel template-free method in supercritical CO₂ as heterogeneous catalysts for epoxidation with H₂O₂

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ABSTRACT

A series of tungsten oxide-silica (WO₃–SiO₂) composite nanomaterials were synthesized through a novel, template-free sol-gel method, in which supercritical-CO₂ (scCO₂) was utilized as synthesis medium. The efficacy of the synthesis method stems from a tailored reactor design that allows the contact of the reactants only in the presence of scCO₂. Selected synthetic parameters were screened with the purpose of enhancing the performance of the resulting materials as heterogeneous catalysts in epoxidation reactions with H₂O₂ as environmentally friendly oxidant. A cyclooctene conversion of 73% with epoxide selectivity of > 99% was achieved over the best WO₃–SiO₂ catalyst under mild reaction conditions (80 °C), equimolar H₂O₂ amount (1:1) and low WO₃ loading (~2.5 wt%). The turnover number achieved with this catalyst (TON = 328), is significantly higher than that of a WO₃–SiO₂ prepared via a similar sol-gel route but without supercritical CO₂, and that of commercial WO₃. A thorough characterization with a combination of techniques (ICP-OES, N₂-physisorption, XRD, TEM, STEM-EDX, SEM-EDX, FT-IR and Raman spectroscopy, XPS, TGA and FT-IR analysis of adsorbed pyridine) allowed correlating the physicochemical properties of the WO₃–SiO₂ nanomaterials with their catalytic performance. The high catalytic activity was attributed to: (i) the very high surface area (892 m²/g) and (ii) good dispersion of the W species acting as Lewis acid sites, which were both brought about by the synthesis in supercritical CO₂, and (iii) the relatively low hydrophilicity, which was tuned by optimizing the tetramethyl ortho-silicate concentration and the amount of basic solution used in the synthesis of the materials. Our optimum catalyst was also tested in the reaction of cyclohexene with H₂O₂, resulting in cyclohexane diol as main product due to the presence of strong Brønsted acid sites in the catalyst, whereas the reaction with limonene yielded the internal epoxide as the major product and the corresponding diol as side product. Importantly, the catalyst did not show leaching and could be reused in five consecutive runs without any decrease in activity.

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1. Introduction

Epoxides are very important chemicals in organic synthesis, because they are employed in the preparation of a broad range of useful products such as epoxy glues, coatings, surfactants, lubricants, plasticizers, flavors for food, cosmetics and pharmaceuticals

[1–3]. Hydrogen peroxide (H₂O₂) is a suitable oxidant for synthesizing epoxides from unsaturated compounds in terms of environmental and economic considerations, because it has a high active oxygen content and generates water as the only by-product [4]. Many metal-based catalytic systems have been developed, in which metallic centers act as acid sites or redox sites, which are responsible for the activation of H₂O₂ towards the epoxidation reaction [5,6]. Various mechanisms have been proposed for metal-catalyzed epoxidations with H₂O₂, which can involve the

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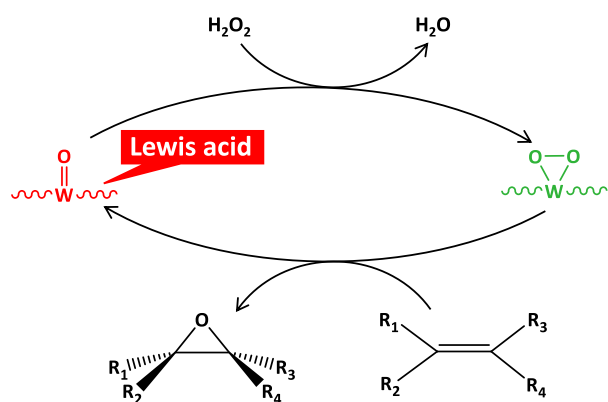
formation of different intermediates (metal-peroxo, metal-hydroperoxo or metal-oxo species) and which can proceed through non-radical or radical pathways (the two might occur alternatively or competitively) [3,7,8]. Among these metal-based catalysts, Ti-based catalysts have been the most widely studied [9–12]. Microporous Ti-based catalysts like TS-1 are only effective in the epoxidation of relatively small, mostly linear substrates with H_2O_2 as the oxidant, while mesoporous Ti-based catalysts are generally reported to be more efficient with an organic oxidant (e.g. *tert*-butyl hydroperoxide) [13], though can perform well also with H_2O_2 if the hydrophobicity of their surface is enhanced [14]. Tungsten-based materials are another class of epoxidation catalysts that has been growingly investigated in recent years [8,15–17]. Tungsten-catalysts exist in many forms, both as homogeneous (e.g. poly-oxotungstate [18,19], poly-oxoperoxotungstate [20], lacunary poly-oxotungstate [21], transition-metal-substituted poly-oxotungstate [22]) and heterogeneous catalysts (e.g. supported W species [16,17], bulk WO_3 [23]). Most W-based epoxidation catalysts are reported to follow a non-radical pathway, in which the W center acts as a Lewis acid site that activates H_2O_2 through the formation of a peroxo intermediate. The following step is the transfer of the oxygen atom to the alkene, leading to the formation of the epoxide product, as illustrated in Scheme 1 [7,8].

In recent years, increasing research efforts have focused on overcoming the inherent limitations related to the separation of homogeneous W-based epoxidation catalysts. For this purpose, heterogeneous analogs of these tungsten-based homogeneous catalysts have been synthesized and tested [16,17,23]. However, leaching of active W species in the presence of H_2O_2 is a major limitation of many claimed W-based heterogeneous catalysts [17]. Different approaches have been explored to tackle this issue, typically involving immobilization of the W-based active species into or onto high surface area materials, thereby stabilizing them e.g. through W–O–Si covalent bonds [24–26]. Another approach consists in preparing nanoparticulate WO_3 by flame spray pyrolysis. The procedure involves the pyrolysis of metal precursors within a combustible solvent by flame spray at high temperature (flame $T > 727^\circ\text{C}$ when oxygen is used) [27]. The obtained nanoparticulate WO_3 displayed remarkably high activity as heterogeneous catalyst for the epoxidation of cyclooctene and could be reused without loss of activity [23], possibly pointing to a low tendency of these nanoparticles to aggregate. However, their small size hampers their separation and recovery. Therefore, in view of a perspective upscaling and industrial application, the immobilization of W species in a high surface area matrix seems a more viable option. In

this context, a commonly used approach consists in grafting W species onto an already-synthesized high surface area support (typically ordered porous silica materials, e.g. MCM-48, SBA-15) [28–32]. The obtained WO_3 -MCM-48,²⁸ WO_3 -SBA-15²⁹ catalysts showed no leaching in cyclooctene epoxidation with H_2O_2 , though the tests were carried out at relative low reaction temperature (30 – 40°C). The stability of the W species against higher reaction temperature was not addressed. Recently, a W/SiO₂ catalyst prepared by grafting of tungsten species on silica by dry impregnation was reported to show good catalytic performance, no leaching but moderate reusability in the epoxidation of limonene and methyl oleate in the presence of H_2O_2 [32]. An alternative approach involves the coprecipitation of W species with silicon precursors such as tetramethyl orthosilicate (TMOS) or tetraethyl orthosilicate (TEOS), typically in the presence of a surfactant, e.g. Pluronic 123 (P123) [26,33], cetyltrimethylammonium bromide (CTABr) [25,34], or cetyltrimethylammonium chloride (CTACl) [35]. The expected formation of W–O–Si bonds in this coprecipitation process has been proposed to avert the leaching problem of W species. For example, a WO_3 -SiO₂ foam material prepared using P123 as template demonstrated good stability up to 60°C in cycloocta-1,5-diene epoxidation [26], while tungsten-modified silica synthesized with CTABr as template was stable at 80°C in styrene epoxidation [25]. In addition, there are also reports on non-hydrolytic coprecipitation procedures that do not require the use of a surfactant while still resulting in materials with high specific surface area (680 – $780\text{ m}^2/\text{g}$) [36]. The prepared W–SiO₂ materials were tested as catalysts for gas-phase metathesis reactions, whereas their catalytic performance and stability in liquid phase reactions (e.g. epoxidations with H_2O_2) were not addressed [36].

Most of the aforementioned grafting and coprecipitation methods involve the use of surfactants as templates to create porous structures with high specific surface area ($> 700\text{ m}^2/\text{g}$) [34,37]. Most surfactants are expensive and typically they are not reusable as they are removed by high temperature calcination, thus limiting the large-scale application of these approaches. Additionally, in both the grafting and coprecipitation methods it is difficult to obtain a uniform dispersion of the W-species and thus to prevent the formation of relatively large tungsten oxide particles, which generally implies a decrease in catalytic activity and an increase in leaching issues [23,26].

On this backdrop, developing a template-free synthesis method for active and stable WO_3 -SiO₂ with high surface area and good dispersion of W species is highly desirable. In this work, we present a novel supercritical carbon dioxide (scCO₂)-assisted sol-gel method to prepare WO_3 -SiO₂ nanomaterials with enhanced activity in the epoxidation of alkenes with H_2O_2 . Sol-gel methods provide a straightforward alternative to template methods, due to their high degree of versatility towards precursors, their mild reaction conditions and easy scale-up [38]. WO_3 -SiO₂ composites have been successfully synthesized by template-free sol-gel methods [25,39–42]. Combining sol-gel methods with drying of the gel in supercritical CO₂ has been reported to yield WO_3 -SiO₂ aerogels (1.3 wt% WO_3) with remarkably high specific surface areas ($1434\text{ m}^2/\text{g}$ after thermal treatment at 200°C and $528\text{ m}^2/\text{g}$ after thermal treatment at 500°C) [43]. Similarly, WO_3 , WO_3 -Al₂O₃ and WO_3 -SiO₂-Al₂O₃ aerogels were synthesized by a sol-gel route followed by scCO₂-drying [44]. These methods exploit the negligible surface tension and ease of separation of supercritical CO₂ to generate high surface area materials [38]. However, the dispersion of tungsten species cannot be adjusted in scCO₂-drying methods. Here, we present a new synthetic strategy in which scCO₂ is not employed as drying agent, but as a solvent. The novelty of this approach lies in the tailored reactor design (Fig. 1, see Experimental section for details), which allows the W and Si precursors and the



Scheme 1. General reaction scheme for the epoxidation of alkenes with H_2O_2 over tungsten-based catalysts.

base to come in contact, and thus to form the $\text{WO}_3\text{--SiO}_2$ materials, only in the presence of the scCO_2 medium. This strategy allows exploiting also other features of supercritical CO_2 such as its high diffusivity and solvating power [38], to promote the formation of $\text{WO}_3\text{--SiO}_2$ nanomaterials with high dispersion of W species and with high specific surface area. The prepared materials displayed high activity as heterogeneous catalysts for the epoxidation of alkenes with H_2O_2 as the oxidant.

2. Materials and methods

2.1. Materials

Tungsten (VI) oxychloride (WOCl_4 , 98.0%), sodium ethoxide solution (21 wt%, ethanol as solvent) and absolute ethanol were used for the preparation of the W precursor for the sol-gel synthesis of $\text{WO}_3\text{--SiO}_2$ in scCO_2 and of the reference material prepared without scCO_2 . Tetramethyl orthosilicate (TMOS, 98%) was used as the Si precursor. 25 wt% ammonia aqueous solution was used as the water and base source in the sol-gel process. Commercially available WO_3 ($\text{WO}_3\text{--Comm}$) was used as a reference catalyst. In epoxidation reactions, *cis*-cyclooctene (95%), cyclohexene (99%) and (R)-(+)-limonene (98%) were used as substrates, while aqueous H_2O_2 (50 wt%) and anhydrous H_2O_2 (26 wt% in ethyl acetate, prepared by ourselves) were employed as oxidant. Ethyl acetate (99.8%), 1,4-dioxane (99.8%, stabilized), 1,3-dioxolane (99%, stabilized), acetonitrile (99.8%), isopropanol (99.5%), ethanol (100%) and methanol (100%) were tested as reaction solvents. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) was used as radical scavenger. Cerium sulfate [$\text{Ce}(\text{SO}_4)_2$] aqueous solution (0.1 M) was used in the titration of H_2O_2 . The ammonia aqueous solution was purchased from Boom, while all the other compounds were purchased from Sigma-Aldrich. All reagents were used without further purification.

2.2. scCO_2 -assisted sol-gel synthesis of $\text{WO}_3\text{--SiO}_2$ materials

The $\text{WO}_3\text{--SiO}_2$ materials were prepared using a scCO_2 -assisted sol-gel method with a novel protocol developed by adapting the synthesis methods of other metal oxides in scCO_2 medium [38,45–48] and by applying them to a sol-gel method inspired by those used in the literature to prepare $\text{WO}_3\text{--SiO}_2$ [43,44]. In order to exploit scCO_2 as reaction medium, we designed a reactor set-up that allows bringing the precursors in contact with each other only during the pressurization to reach scCO_2 conditions. The reactor set-up is based on the use of an in-house developed glass vessel equipped with two cups fixed on the inner wall of the vessel, a magnetic stirring bar and a screw cap containing a silicone/polytetrafluoroethylene (PTFE) septum (Fig. S1A). The synthesis of the $\text{WO}_3\text{--SiO}_2$ materials was performed in a high-throughput scCO_2

reactor unit constructed by Integrated Lab Solutions GmbH (ILS), which contains two modules: (1) a batch reactor equipped with a borosilicate glass window to allow monitoring the reaction visually; and (2) a block containing 10 individually stirred batch reactors, which allows performing 10 reactions simultaneously (Fig. S1A). The two modules can be operated separately or used simultaneously. Each batch reactor has a volume of 84 mL with 30 mm internal diameter and can be operated in a pressure range of 1–200 bar and a temperature range of 20–200 °C. The customized glass vessel described above was designed to fit into these batch reactors (see Fig. S1A). The reactors were pressurized by means of an ISCO pump, heated with electric heating elements and cooled with a water circulation system. Each reactor is equipped with a rupture disk to prevent the risk of overpressure.

We aimed at preparing $\text{WO}_3\text{--SiO}_2$ materials with 2.0 wt% W loading (corresponding to 2.5 wt% WO_3 loading). The $\text{WO}_3\text{--SiO}_2$ materials prepared in this work differ in terms of synthesis parameters. The theoretical yield in the synthesis of all these $\text{WO}_3\text{--SiO}_2$ materials was set to 300.0 mg. The amounts of precursors were calculated based on these general settings. The synthesis of all $\text{WO}_3\text{--SiO}_2$ materials started with the preparation of the W precursor ($\text{WO}(\text{OEt})_4$ in ethanol), following a reported protocol [44]. Briefly, WOCl_4 (11.4 mg) was weighed in a glass vessel equipped with a magnetic stirring bar and a screw cap containing a silicone/PTFE septum in a glove box under N_2 atmosphere because of its highly hygroscopic nature. Then, a 21 wt% solution of sodium ethoxide in ethanol (41.5 mg) and absolute ethanol (240.0 mg) were mixed under a fume hood, and this solution was added dropwise with a syringe needle to the closed vessel containing WOCl_4 under continuous stirring. NaCl was formed as a white solid product, as a consequence of the concomitant formation of $\text{WO}(\text{OEt})_4$. After stirring at room temperature for 2 h, the NaCl precipitate was removed by centrifugation (4000 rpm, 20 min) and the supernatant ethanol solution containing $\text{WO}(\text{OEt})_4$ was labeled as W-prec. In aqueous sol-gel processes, the reactivity of tungsten ethoxide with water is much higher than that of silicon alkoxides, thus tending to generate separate WO_3 and SiO_2 phases [43]. To avoid this, in this work the most reactive silicon alkoxide (i.e. TMOS) was chosen as Si precursor and prehydrolyzed, with the purpose of compensating as much as possible for the difference in hydrolysis rate between W and Si precursors. A similar prehydrolysis strategy has been reported for the preparation of $\text{WO}_3\text{--Al}_2\text{O}_3$ or $\text{WO}_3\text{--Al}_2\text{O}_3\text{--SiO}_2$ [44] and $\text{V}_2\text{O}_5\text{--TiO}_2$ [49]. The prehydrolysis step involved the dissolution of TMOS (756.0 mg, 4.875 mmol) in ethanol, followed by addition of a 25 wt% aqueous solution of ammonia (referred to as 'basic solution'). The amounts of ethanol and basic solution were tuned using a systematic approach (see Table 1) with the purpose of optimizing the synthesis of the $\text{WO}_3\text{--SiO}_2$ materials towards their activity as epoxidation

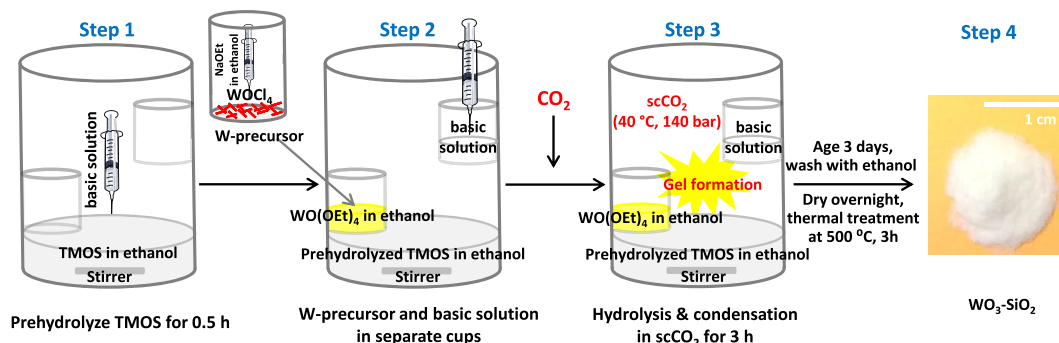


Fig. 1. Scheme of the synthesis of $\text{WO}_3\text{--SiO}_2$ materials by scCO_2 -assisted sol-gel method in a customized glass vessel (the cap of the vessel is not shown).

catalysts. Three ethanol amounts were used, *i.e.* 4284.0 mg, 3024.0 mg, and 2268.0 mg, corresponding to 15 wt%, 20 wt%, and 25 wt% TMOS in ethanol. Four basic solution amounts were employed, *i.e.* 86.0 mg, 172.0 mg, 258.0 mg, and 344.0 mg. The obtained mixture, referred to as Si-prec, varied in appearance from a clear solution to an opaque sol as a function of the amounts of ethanol and basic solution employed. The Si-prec mixture was prepared at the bottom of the customized vessel (see Fig. 1, step 1) and stirred (800 rpm) at room temperature for 30 min. Next, an equal amount of basic solution as that used for the prehydrolysis of TMOS was weighed and transferred with a syringe needle to the upper cup of the vessel. Then, W-prec was transferred to the lower cup of the vessel. The septum of the vessel was pierced with two syringe needles to allow CO₂ to flow in and out of the vessel. Then, the vessels were placed into the batch reactors, the block was subsequently closed and stirring (800 rpm) was started immediately. Next, the reactors were firstly pressurized with CO₂ to 60 bar, then heated up to 40 °C, followed by a second pressurization with CO₂ to 140 bar (this process takes around 1.5 h). The applied conditions are above the critical point of CO₂ ($T_c = 31.1$ °C, $p_c = 7.38$ MPa). During this pressurization step, the mixtures placed in the different compartments of our customized vessel are brought in contact with each other (as visually monitored when the experiments were carried out in the reactor with the borosilicate glass window). After reaching these conditions, the reaction mixtures were continuously stirred for 3 h. Next, the stirring was stopped, the block was cooled down to 20 °C and CO₂ was removed slowly with an average depressurization rate of 1.5 bar/min. The whole procedure described above takes 8–9 h. After reaching atmospheric pressure, the obtained mixtures were aged in the original vessels for 3 days. Then, they were washed thoroughly with ethanol for three times under centrifugation (4000 rpm, 20 min), followed by drying at 80 °C for 12 h and thermal treatment in a calcination oven at 500 °C for 3 h (heating rate: 3 °C/min). This calcination temperature is only slightly above the temperature (450 °C) at which amorphous WO₃ starts to convert into the crystalline form [50]. The whole preparation procedure is summarized in Fig. 1. The synthesized WO₃–SiO₂ materials were named as WO₃–xSiO₂–y, where x is the wt% of TMOS in ethanol used as Si precursor (x = 15, 20, 25) and y is the molar ratio between ammonia and Si + W (y = 0.25, 0.5, 0.75, 1).

A reference WO₃–SiO₂ material (WO₃–SiO₂–Ref) was synthesized with a similar procedure to that used to prepare WO₃–20SiO₂–0.5 (our optimum catalyst), but without the use of scCO₂. Briefly,

the preparation of the W precursor was the same as that for WO₃–20SiO₂–0.5. Then, 756.0 mg TMOS was dissolved in 3024.0 mg ethanol upon stirring in a round-bottom flask. Then, 172 mg of the 25 wt% aqueous solution of ammonia was added to the solution and the reaction mixture was stirred at room temperature for 30 min. Next, the reaction mixture was heated up to 40 °C. Afterwards, the W precursor and 172 mg of the 25 wt% aqueous solution of ammonia were added dropwise with separate syringe needles to the prehydrolyzed TMOS in 30 min under continuous stirring. After stirring at 40 °C for 3 h, the obtained mixture was cooled down, aged, washed, dried, and thermally treated following the same procedure used for WO₃–20SiO₂–0.5. Another reference catalyst with 1.3 wt% WO₃ was also synthesized (see Supporting Information).

2.3. Characterization

Elemental analysis was carried out by inductively coupled plasma optical emission spectroscopy (ICP-OES) on a Perkin Elmer Optima 7000 DV instrument. Before the analysis, the samples were dissolved using a mixture of hydrofluoric acid (HF) and nitric acid (HNO₃). N₂-physisorption isotherms were recorded on a Micromeritics ASAP 2420 apparatus at –196 °C. The samples were degassed under reduced pressure (≤ 133 μ bar) at 200 °C for 5 h before N₂ adsorption. The specific surface area was evaluated with the Brunauer–Emmett–Teller (BET) method. It should be noted that the measurement of the specific surface area typically has an intrinsic experimental error of about 5%. X-ray diffraction patterns (XRD) were recorded on a Bruker D8 Phaser diffractometer operated with Cu K α radiation ($\lambda = 1.5406$ Å). XRD patterns were measured in reflection geometry in the 2 θ range between 10 and 80° with 0.02° and a counting time of 0.5 s for each step. Transmission electron microscopy (TEM) images were collected on a Philips CM12 microscope operating at 120 keV. The scanning transmission electron microscopy (STEM) and energy-dispersive X-ray (EDX) spectroscopy mapping were carried out on an FEI Tecnai T20 electron microscope operating at 200 keV, equipped with an X-Max 80T SDD detector (Oxford Instruments). For the preparation of the TEM/STEM samples, the powder sample was dispersed in ethanol by sonication for 20 min and then deposited on a holey carbon-coated copper grid. Scanning electron microscopy (SEM) and SEM-EDX analysis was performed on a Philips XL30 ESEM microscope operating at 20 keV. The SEM samples were prepared by dispersing the powder sample on a carbon tape and gold was

Table 1
Selected physicochemical properties and catalytic performance of WO₃–SiO₂ materials prepared with different synthetic parameters.

Entry	Catalyst	Synthesis			Physicochemical properties			Catalytic performance ^a		
		TMOS Conc. (wt%)	Base/(W + Si) ratio	Yield of Catalyst Synthesis (%)	W (wt%) ^b	Specific surface area (m ² /g)	Adsorbed H ₂ O (nH ₂ O/nm ²)	Alkene Conv. (%)	Epoxide Yield (%)	TON ^c
1	WO ₃ –15SiO ₂ –0.25	15	0.25	> 40	4.8	–	–	62	60	115
2	WO ₃ –15SiO ₂ –0.5	15	0.5	> 90	2.0	642	5.8	36	36	169
3	WO ₃ –15SiO ₂ –0.75	15	0.75	> 90	1.8	723	14.8	27	27	139
4	WO ₃ –15SiO ₂ –1	15	1	> 90	2.1	609	19.1	25	25	108
5	WO ₃ –20SiO ₂ –0.25	20	0.25	~ 50	3.5	–	–	67	63	165
6	WO ₃ –20SiO ₂ –0.5	20	0.5	> 90	2.1	892	3.1	62	62	278
7	WO ₃ –20SiO ₂ –0.75	20	0.75	> 90	2.0	1074	4.1	44	44	201
8	WO ₃ –20SiO ₂ –1	20	1	> 90	1.8	315	13.0	43	43	216
9	WO ₃ –25SiO ₂ –0.25	25	0.25	~ 55	2.1	–	–	62	62	277
10	WO ₃ –25SiO ₂ –0.5	25	0.5	> 90	2.0	667	2.1	60	60	283
11	WO ₃ –25SiO ₂ –0.75	25	0.75	> 90	1.9	728	3.2	44	44	210
12	WO ₃ –25SiO ₂ –1	25	1	> 90	2.0	313	5.7	29	29	133

^a Reaction conditions: 2 mmol cyclooctene, 2 mmol 50 wt% aqueous H₂O₂, 1 mmol di-*n*-butyl-ether, 250 mg isopropanol, 2.0 g ethyl acetate, 40 mg catalyst, 80 °C, 4 h.

^b W loadings determined by ICP-OES analysis (theoretical W loading: 1.97 wt%).

^c Turnover number (TON), defined as mol_{alkene,converted}/mol_W calculated after 4 h of reaction.

sputter-deposited to improve the conductivity of the sample surface. Fourier Transform infrared spectroscopy (FT-IR) measurements were performed on an IRTTracer-100 spectrometer by averaging 64 scans with a spatial resolution of 4 cm^{-1} . The background spectrum was recorded using an empty cell. Raman spectra were recorded at $\lambda_{\text{exc}} = 785\text{ nm}$ using a Perkin Elmer Raman Station 400 F at room temperature. The hydrophilicity of the catalysts was evaluated by thermogravimetric analysis (TGA) on a Perkin Elmer TGA 4000 instrument under N_2 atmosphere with a heating rate of $10\text{ }^\circ\text{C/min}$. The freshly calcined $\text{WO}_3\text{-SiO}_2$ samples were allowed to reach the maximum degree of water adsorption by an overnight pre-treatment in a desiccator containing a saturated NH_4Cl aqueous solution. The average number of water molecules adsorbed per nm^2 of the surface of the catalyst was estimated from the mass loss between 25 and $150\text{ }^\circ\text{C}$ using the following equation [51]:

$$n_{\text{H}_2\text{O}} = \frac{\Delta m}{m_i} \times \frac{N_A}{A_{\text{BET}} M_{\text{H}_2\text{O}}}$$

where Δm is the mass loss between 25 and $150\text{ }^\circ\text{C}$ (g); m_i is the initial mass of the sample at $25\text{ }^\circ\text{C}$ (g); N_A is the Avogadro constant ($6.022 \times 10^{23}\text{ mol}^{-1}$); A_{BET} is the specific surface area of the sample (nm^2/g); $M_{\text{H}_2\text{O}}$ is the molar mass of water (18.0153 g/mol). This measurement was repeated for two times for each material (the deviation was within $\pm 3\%$) and the average values obtained from two tests were reported. X-ray photoelectron spectroscopy (XPS) analysis was performed using a Surface Science SSX-100 ESCA instrument with a monochromatic Al $K\alpha$ X-ray source ($h\nu = 1486.6\text{ eV}$). Substrates consisting of 200 nm Au on mica were prepared by sublimation of 99.99% Au (Schöne Edelmetaal B.V.) on freshly cleaved mica, kept previously at $375\text{ }^\circ\text{C}$ for 16 h in order to remove impurities in a custom-built high-vacuum evaporator (base pressure: 10^{-7} mbar). The sample was deposited on the gold surface by drop-casting and introduced immediately into the spectrometer. The pressure in the measurement chamber was maintained below $1 \times 10^{-9}\text{ mbar}$. The electron take-off angle with respect to the surface normal was 37° . The XPS data were acquired by using a spot size of $600\text{ }\mu\text{m}$ diameter and the energy resolution was set to 1.3 eV for both the survey spectra and the detailed spectra of the $\text{W}4f$, $\text{W}4d$, $\text{O}1s$, $\text{Si}2p$ and $\text{C}1s$ core level regions. During the XPS measurements, an electron flood gun was used to compensate for charging. All XPS spectra were analyzed using the least-squares curve-fitting program Winspec [52]. Deconvolution of the spectra included a Shirley [53] baseline subtraction and fitting with a minimum number of peaks consistent with the chemical structure of the sample, taking into account the experimental resolution. The profile of the peaks was taken as a convolution of Gaussian and Lorentzian functions. Binding energies deduced from fits have an uncertainty of $\pm 0.1\text{ eV}$ and are referenced to the $\text{C}1s$ photoemission peak centered at 284.8 eV [54]. The larger full width at half maximum (FWHM) of the $\text{W}4d$ signal does not stem from charging effect, as indicated by the absence of an extra component (of the same relative intensity) due to charging in all other XPS peaks. The uncertainty in the peak intensity determination is 2% for all core levels reported. The acidity of the $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ catalyst was investigated using FT-IR analysis of adsorbed pyridine. The spectra were recorded on a Bruker Vertex 70 FT-IR spectrometer equipped with a LN-MCT detector in the range $1400\text{--}1700\text{ cm}^{-1}$. Each spectrum was collected with a resolution of 4 cm^{-1} . The sample was prepared in the form of a self-supporting disk. The sample was firstly pre-treated at $400\text{ }^\circ\text{C}$ for 1 h under reduced pressure (0.006 mbar) and then cooled down to room temperature. During cooling down, the sample reference spectra were recorded at $350/250/150\text{ }^\circ\text{C}$. Then, pyridine vapor (12 mbar) was introduced into the system at room temperature for 30 min ,

after which the sample was evacuated at room temperature for 30 min to remove physisorbed pyridine. The evacuated samples were subjected to desorption at $150/250/350\text{ }^\circ\text{C}$ for 30 min , with a heating rate of $4\text{ }^\circ\text{C/min}$, and the FT-IR spectra were recorded at each temperature.

2.4. Catalytic tests

The epoxidation of alkenes with H_2O_2 over the $\text{WO}_3\text{-SiO}_2$ catalysts was carried out in glass vessels (equipped with stirrers and screw caps) that fit into a 48-well high-throughput reaction block equipped with heating and stirring units, which allows performing up to 48 tests simultaneously (Fig. S1B). In a typical catalytic test, 2 mmol alkene, 1 mmol di-*n*-butyl ether (as gas chromatography (GC) internal standard), 250 mg 2-propanol (as cosolvent, to promote the formation of a monophasic liquid reaction mixture) and 2.0 g solvent were firstly weighed in the glass vessel. Then, 2 mmol 50 wt\% aqueous H_2O_2 and 40 mg $\text{WO}_3\text{-SiO}_2$ catalyst were added. Then, the glass vial was closed with a screw cap and placed into the 48-well reaction block. Next, the reaction mixture was stirred (800 rpm) at $80\text{ }^\circ\text{C}$ for 4 h , after which the stirring was stopped and the reaction mixture was centrifuged for 5 min at 4000 rpm to deposit the catalyst. The supernatant was analyzed by means of gas chromatography (GC) using an Agilent Technologies 7980B GC equipped with an Agilent DB-5#6 (5% -phenyl)-methylpolysiloxane column (15 m , $320\text{ }\mu\text{m ID}$). The identification of the by-products was performed by GC-mass spectrometry (GC-MS) on an HP 6890 Series GC equipped with a Restek Rxi-5Si MS fused silica column (30 m , $250\text{ }\mu\text{m ID}$) coupled to an HP 5973 Mass Selective Detector. The formulae for calculating the moles of substrates obtained from GC measurement and, based on these values, the conversion of alkenes (Conv.), the yield and selectivity (Sel.) towards the epoxides, the turnover number (TON) and turnover frequency (TOF) of the catalyst, the efficiency in the utilization of H_2O_2 are listed in the Supporting Information. The catalytic results showed high reproducibility in duplicate tests (deviation in the epoxide yield value within $\pm 2\%$). For these experiments, the average value of the epoxide yield is reported. *Safety note:* hydrogen peroxide and ethers (e.g. 1,4-dioxane and 1,3-dioxolane) can form explosive peroxides unless they contain stabilizers (as it is the case for the ethers used in this work).

Leaching and recycling tests were performed using the optimum catalyst under the optimum reaction conditions. For the leaching test, after reacting at $80\text{ }^\circ\text{C}$ for 0.5 h , the reaction mixture was centrifuged for 5 min at 4000 rpm to deposit the catalyst. The supernatant was filtered with a $0.45\text{ }\mu\text{m}$ filter connected to a syringe. Then, a small aliquot of the filtrate was immediately analyzed by GC and the residual liquid was stirred at $80\text{ }^\circ\text{C}$ for 3.5 h , after which it was also analyzed by GC. The presence or absence of leached active sites was determined from the difference in alkene conversion and epoxide yield between the liquid after 0.5 h and the one after 4 h . For the recycling tests, after reacting at $80\text{ }^\circ\text{C}$ for 4 h , the catalyst was transferred into a centrifuge tube, deposited by centrifugation at 4000 rpm for 5 min , followed by removal of the supernatant with a pipette. Next, around 40 mL of 1,4-dioxane was added to the centrifuge tube and the tube was shaken vigorously. Then, the tube was centrifuged at 4000 rpm for 30 min , after which the supernatant was removed again. This washing procedure was repeated five times. Then, the catalyst was dried at $105\text{ }^\circ\text{C}$ for 12 h and regenerated by thermal treatment at $500\text{ }^\circ\text{C}$ for 3 h (heating rate: $3\text{ }^\circ\text{C/min}$) before reuse.

The study of the effect of the type of H_2O_2 was carried out by comparing the catalytic performance with 50 wt\% aqueous H_2O_2 to that with 26 wt\% anhydrous H_2O_2 in ethyl acetate, which was prepared by removing water from the homogeneous solution of

12 mL of 50 wt% aqueous H_2O_2 and 170 mL of ethyl acetate by means of a Dean-Stark trap at 93 °C. *Safety note:* care should be taken when using anhydrous H_2O_2 in a flammable organic solvent (explosive) [55]. The Dean-Stark trap was placed in a fume hood to release the oxygen and the possibly explosive gas mixture of oxygen and solvent generated by possible H_2O_2 decomposition. A rubber cap was placed on top of the condenser instead of a glass cap to prevent the risk of accidents in case of blowing up of the cap caused by pressure build-up from H_2O_2 decomposition.

3. Results and discussion

A novel synthesis method for preparing $\text{WO}_3\text{--SiO}_2$ materials with high specific surface area and highly dispersed W species in the silica matrix was designed by employing supercritical CO_2 as reaction medium. Our approach is based on the use of a tailored reactor that allows the reactants (solutions containing the W and Si precursors and a basic aqueous solution) to come in contact, and thus to form the $\text{WO}_3\text{--SiO}_2$ materials, only in the presence of the scCO_2 medium.

3.1. Synthesis and catalytic testing of the $\text{WO}_3\text{--SiO}_2$ materials

Our study started with the preparation of the $\text{WO}_3\text{--SiO}_2$ materials by a scCO_2 -assisted sol-gel method in which selected synthetic parameters were systematically varied (*i.e.* TMOS concentration and basic solution amount, see Table 1). The nominal loading of WO_3 was kept constant at 2.5 wt% (*i.e.* 2.0 wt% of W). This value was chosen with the aim of preparing materials in which the W loading is sufficiently high to reach a high catalytic activity per gram of material, while granting a high dispersion of the W-based active species in the SiO_2 matrix, which is expected to stabilize them against leaching in the presence of aqueous hydrogen peroxide.

The synthesis of the $\text{WO}_3\text{--SiO}_2$ catalysts with our scCO_2 -assisted method typically gives very high yield of material (> 90% of the theoretical value), although the $\text{WO}_3\text{--SiO}_2$ prepared using the minimum amount of basic solution (Table 1, entries 1, 5, 9) gave lower yield ($\leq 55\%$). This can be explained considering that during the synthesis, after removing CO_2 (*i.e.* at the end of step 3 in Fig. 1), the reaction mixtures prepared using higher amounts of basic solution formed an extensive gel, whereas those prepared with the minimum amount of basic solution consisted of a small amount of gel at the bottom and a viscous supernatant liquid, indicating a lower degree of progress in the hydrolysis-condensation of the precursors. The viscous supernatant containing W or Si species was removed and discarded in the washing step, thus leading to the observed low yield of $\text{WO}_3\text{--SiO}_2$ materials. Additionally, samples from entries 1 and 5 were found to have much higher loading of W compared to the theoretical value (2.0 wt%), indicating that under these conditions the degree of condensation of the Si species was lower compared to the W species.

The prepared $\text{WO}_3\text{--SiO}_2$ materials were tested as heterogeneous catalysts in the epoxidation of cyclooctene with a stoichiometric ratio of H_2O_2 (1:1) at 80 °C. All the prepared $\text{WO}_3\text{--SiO}_2$ catalysts proved to be active and selective epoxidation catalysts, with the performance varying significantly as a function of the parameters used in the synthesis of the materials (Table 1). When comparing the activity of the $\text{WO}_3\text{--SiO}_2$ catalysts prepared with the same concentration of TMOS solution (*e.g.* Table 1, entries 1–4), the highest cyclooctene conversion was always obtained with the catalyst prepared with the lowest amount of basic solution ($\text{base}/(\text{W} + \text{Si}) = 0.25$, entries 1, 5, 9). When comparing the activity among $\text{WO}_3\text{--SiO}_2$ catalysts prepared with the same amount of basic solution (*e.g.* Table 1, entries 2, 6, 10), the highest cyclooctene

conversion was always reached over the catalysts prepared with 20 wt% TMOS solution (entries 5–8). Combining these two observations, the $\text{WO}_3\text{--}20\text{SiO}_2\text{--}0.25$ catalyst prepared with $\text{base}/(\text{W} + \text{Si}) = 0.25$ and a 20 wt% TMOS as Si-prec (entry 5) gives the highest cyclooctene conversion (67%). However, this catalyst is not fully selective towards the epoxide product and besides cyclooctene oxide (63% yield), cyclooctane diol was observed as side product (4% yield). The formation of the diol is an indication of the presence of Brønsted acid sites that can catalyze the hydrolysis of the formed epoxide [17]. This is most likely related to the higher W loading present in this catalyst (3.5 wt%), as suggested by the fact that the only other catalyst that led to a non-negligible formation of cyclooctane diol (2%) was $\text{WO}_3\text{--}15\text{SiO}_2\text{--}0.25$ (entry 1), which also has a relatively high W loading (4.8 wt%). On the other hand, virtually complete epoxide selectivity (> 99%) was obtained with other $\text{WO}_3\text{--SiO}_2$ catalysts with lower W loadings (around the theoretical value of 2.0 wt%), among which the $\text{WO}_3\text{--}20\text{SiO}_2\text{--}0.5$ catalyst (entry 6) gives the highest cyclooctene conversion (62%), with a TON of 278 and a TOF of 70 h^{-1} . However, it should be noted that the catalyst prepared with $\text{base}/(\text{W} + \text{Si}) = 0.5$ and a 25 wt% TMOS as Si-prec (entry 10) displayed an analogous performance. Since the yields in the synthesis of the $\text{WO}_3\text{--SiO}_2$ materials prepared with the minimum amount of basic solution were not optimal and, in the case of $\text{WO}_3\text{--}15\text{SiO}_2\text{--}0.25$ and $\text{WO}_3\text{--}20\text{SiO}_2\text{--}0.25$, the epoxide selectivity was not complete, these three catalysts were not investigated further (Table 1, entries 1, 5, 9).

To investigate if a lower W loading could be beneficial to the catalytic activity (in terms of TON), a $\text{WO}_3\text{--SiO}_2$ catalyst with a 1.3 wt% WO_3 loading was synthesized. However, the catalytic test over this catalyst gave a much lower cyclooctene conversion and a lower TON than those of the $\text{WO}_3\text{--}20\text{SiO}_2\text{--}0.5$ catalyst (for further details, see the Supporting Information). Therefore, it was concluded that a 2.5 wt% WO_3 loading represents the optimum for our scCO_2 -assisted synthesis method. Among the prepared catalysts with this loading, $\text{WO}_3\text{--}20\text{SiO}_2\text{--}0.5$ displayed the highest epoxide yield, accompanied with full selectivity and high TON. Therefore, this material was selected for further study.

When employing hydrogen peroxide as oxidant, it is important to estimate to what extent the catalyst is able to promote the desired epoxidation reaction against the competitive decomposition of H_2O_2 into H_2O and O_2 . For this purpose, the amount of remaining H_2O_2 after the test with the $\text{WO}_3\text{--}20\text{SiO}_2\text{--}0.5$ catalyst was titrated with a 0.1 M solution of cerium sulfate [$\text{Ce}(\text{SO}_4)_2$], following a reported protocol [56]. The titration indicated that 13% of the initial amount H_2O_2 was still present after reaction, which corresponds to a 25% decomposition and thus to a 71% efficiency in the utilization of H_2O_2 .

Next, the reaction conditions (*i.e.* solvent, H_2O_2 type) were optimized with the aim of maximizing the epoxide yield over the $\text{WO}_3\text{--}20\text{SiO}_2\text{--}0.5$ catalyst. The selected solvent should be able to form a single phase with a mixture of cyclooctene, 50 wt% aqueous H_2O_2 solution, internal standard and cosolvent, thus avoiding the mass transfer problems that would be associated with a biphasic liquid system. Based on these considerations, a set of solvents (*i.e.* acetonitrile, 1,3-dioxolane, 1,4-dioxane, methanol, ethanol and isopropanol) of either aprotic or protic nature and with different polarities were screened as alternative solvents to ethyl acetate in the epoxidation of cyclooctene with H_2O_2 , while keeping all other reaction conditions constant. Selected physical properties of these solvents are listed in Table S1. Additionally, solvents with low toxicity, low environmental impact, low flammability and explosion risks are preferable. According to the CHEM21 guide for ranking the safety and greenness of solvents [57], the selected alcohols and ethyl acetate are recommended solvents, acetonitrile is labeled as a problematic solvent, and 1,4-dioxane and 1,3-dioxolane

need to contain stabilizers (as is the case in this work) to avoid being labeled as hazardous solvents due to safety concerns (see experimental section). The catalytic tests clearly indicate that the catalytic activity of $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ is higher in aprotic solvents (Fig. 2). The worse performance of protic solvent can be related to the competitive coordination of the protic solvent molecules and H_2O_2 to the tungsten centers, which would hinder the activation of H_2O_2 [9,58,59]. When comparing the catalytic performance of the $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ catalyst as a function of polarity, the activity increased with decreasing dielectric constant value within each class of solvents (aprotic or protic). Highly polar solvents might lead to lower catalytic performance because they can hamper the access of the apolar cyclooctene to the catalyst surface [60]. Combining these two considerations, the $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ catalyst demonstrated the highest catalytic activity in terms of cyclooctene conversion (73%), cyclooctene oxide yield (73%) and TON (328) in the most apolar among the tested aprotic solvents (1,4-dioxane).

With the aim of further decreasing the polarity of the reaction mixture, anhydrous H_2O_2 (26 wt% in ethyl acetate) was tested as an alternative to aqueous H_2O_2 . However, the cyclooctene conversion dropped to 23% under these conditions, which is most likely due to the difficult access of the polar, hydrophilic H_2O_2 to the catalyst surface when the latter is covered with an apolar solvent. It can be concluded that the polarity of the reaction mixture should be carefully tuned to ensure a good contact of both alkene and hydrogen peroxide - which have markedly different polarity - with the catalyst surface.

When the catalytic test was performed with half the amount of the $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ catalyst (20 mg) in 1,4-dioxane as solvent, a cyclooctene conversion of 35% was obtained, which is around half of that obtained with 40 mg of the $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ catalyst (73%), thus excluding external diffusion limitations in the tests performed with 40 mg of catalyst. Importantly, a leaching test with $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ proved the true heterogeneity of the catalyst as no further increase of the cyclooctene conversion and epoxide yield was observed after hot-filtration to remove the catalyst after 0.5 h and letting the solution react for further 3.5 h (see Fig. S2). The catalyst was also highly reusable after washing and regeneration by thermal treatment, showing no obvious loss of activity in five consecutive runs (see Fig. S3).

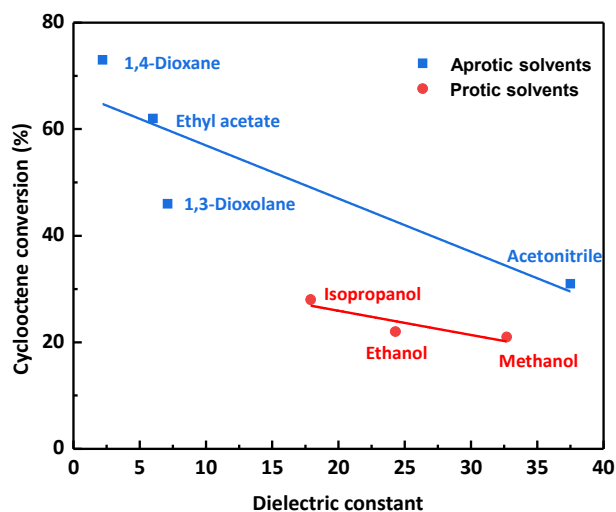


Fig. 2. Cyclooctene conversion over the $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ catalyst as a function of the dielectric constant of aprotic (blue) and protic (red) solvents. Reaction conditions as in Table 1.

Additionally, in order to gain more insight on how the $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ catalyst activates H_2O_2 towards the epoxidation reaction, a control experiment was conducted under the optimum reaction conditions but with the addition of a radical scavenger (TEMPO, 1 mol% relative to H_2O_2). No difference in cyclooctene oxide yield was observed with or without adding TEMPO, thus indicating that under the employed conditions the $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ catalyst follows a non-radical pathway. This strongly suggests that the epoxidation proceeds through the formation of peroxo intermediates (see Scheme 1) over the Lewis acid sites of the $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ catalyst, in analogy to several previously reported W-based catalysts for epoxidation reactions [8,15–23].

3.2. Catalyst characterization

With the purpose of correlating the good catalytic performance and stability of $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ to its physicochemical properties and of comparing it with other $\text{WO}_3\text{-SiO}_2$ catalysts, we performed a characterization study by a combination of different techniques. The N_2 -physisorption isotherms of all the $\text{WO}_3\text{-SiO}_2$ materials display a type IV isotherm with a hysteresis loop at high p/p^0 value, indicating the presence of inter-particle void spaces at the mesopore scale in these materials. The isotherm of the optimum catalyst ($\text{WO}_3\text{-20SiO}_2\text{-0.5}$) is shown in Fig. 3A. The $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ catalyst displayed the second highest specific surface area ($892 \text{ m}^2/\text{g}$), slightly lower than that of $\text{WO}_3\text{-20SiO}_2\text{-0.75}$ ($1074 \text{ m}^2/\text{g}$), and with both of them being significantly higher than that ($400 \text{ m}^2/\text{g}$) of a $\text{WO}_3\text{-SiO}_2$ material reported in literature [25], which was prepared with a similar W loading and the same thermal treatment temperature, but in the presence of a template and without scCO_2 . These results demonstrate that the dispersion of the tungsten species in a silica matrix using our scCO_2 -assisted method leads to material with high specific surface area, which is a good foundation to grant that a large fraction of the W-sites are exposed on the surface of the material, particularly when compared to unsupported bulk WO_3 materials (e.g. commercial tungsten oxide, $\text{WO}_3\text{-Comm}$, has an extremely low surface area of $3 \text{ m}^2/\text{g}$).

For catalytic applications, the high specific surface area should be ideally combined with a structure that provides unrestricted accessibility to the active sites for reactants and easy removal of the products. In our case, this is proven by TEM analysis, which reveals that $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ consists of irregular primary nanoparticles with sizes in the 10–30 nm range (Fig. 4A). In some zones of the TEM images, the nanoparticles form aggregates, though these might not be structural and just be caused by inadequate dispersion of the material in ethanol during the preparation of the TEM sample. Virtually no lattice fringe of crystalline WO_3 could be found in the sample; an example of the very rare crystalline domains ($< 10 \text{ nm}$) is shown in Fig. S4. The spacing of the magnified lattice fringes is around 0.384 nm , which corresponds to the (002) plane of WO_3 [61]. This observation is in line with the XRD pattern of $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ (Fig. 3B), which shows only low-intensity peaks stemming from crystalline WO_3 at 23.2° and 33.4° , corresponding to the (002) and (022) planes of the monoclinic phase. The broad peak in the $2\theta = 15\text{--}30^\circ$ range is characteristic for amorphous silica [39]. When comparing the XRD patterns of the $\text{WO}_3\text{-SiO}_2$ catalysts prepared by our scCO_2 -assisted method, it can be inferred that the materials with the highest catalytic activity ($\text{WO}_3\text{-20SiO}_2\text{-0.5}$ and $\text{WO}_3\text{-25SiO}_2\text{-0.5}$, see Table 1) are also those with the lowest degree of crystallinity (see Fig. S5). This low degree of crystallinity is desirable as it would imply a high dispersion of the W-species and, consequently, a high fraction of W atoms being involved in W–O–Si bonds, which were anticipated to prevent the leaching of W species. The good dispersion of W within the $\text{WO}_3\text{-20SiO}_2\text{-0.5}$ material was further proven by elemental mapping with either

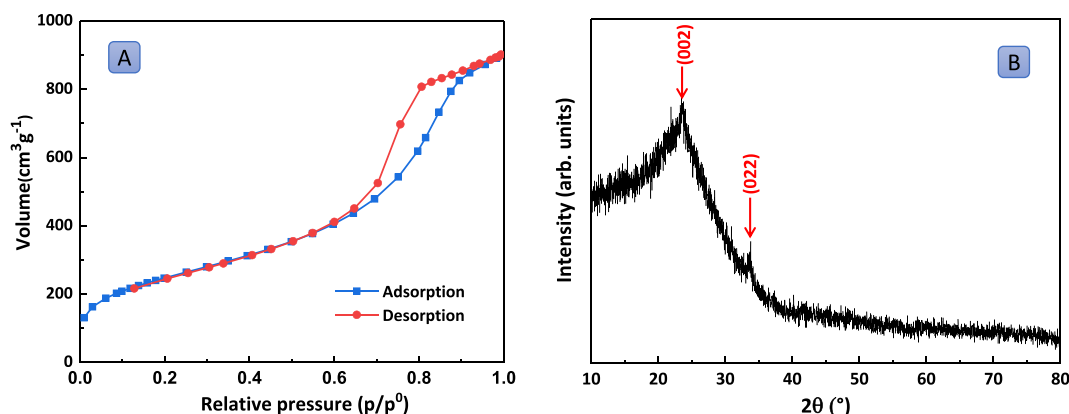


Fig. 3. (A) N_2 adsorption-desorption isotherms and (B) XRD pattern of $WO_3-20SiO_2-0.5$.

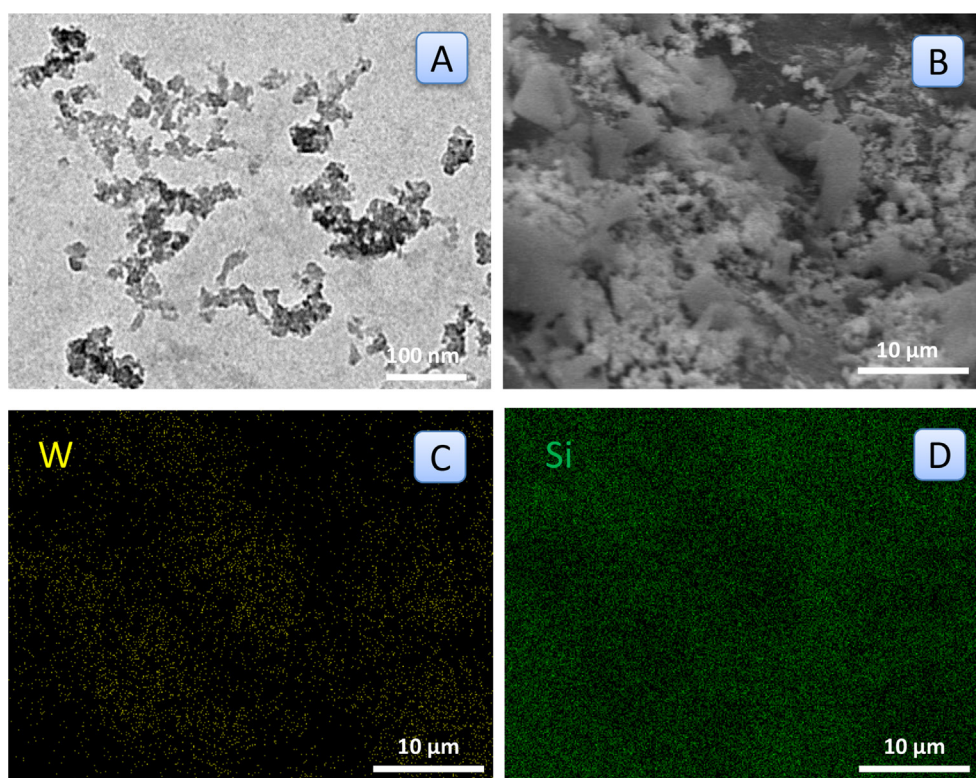


Fig. 4. TEM (A) and SEM (B) images of $WO_3-20SiO_2-0.5$. SEM-EDX elemental mapping of W (C) and Si (D).

TEM-EDX (Fig. S4B) or SEM-EDX (Fig. 4B, C, D), which demonstrate a relatively intimate mixing of tungsten and silicon at the nanoscale, although some areas with higher concentration of W than others can be observed at the micrometre scale.

The expected presence of W–O–Si bonds was monitored by FT-IR and Raman spectroscopy. In the FT-IR spectrum of $WO_3-20SiO_2-0.5$ (Fig. 5A), the prominent peak around 1041 cm^{-1} (Δ) with a shoulder at around 1225 cm^{-1} (θ) corresponds to typical stretching vibrations of Si–O–Si bonds [25,29]. The peak at 802 cm^{-1} (\circ) is assigned to the stretching vibrations of Si–O–Si [25,42] and/or W–O–W bonds [40] (as observed in the spectrum of WO_3 -Comm, provided here as a reference). The shoulder at 963 cm^{-1} (α) is ascribed to the vibrations of W species incorporated into silica and is thus an indication of the formation of W–O–Si bonds [25,33].

The broad absorption peak at $3200\text{--}3600\text{ cm}^{-1}$ is attributed to the –OH stretching vibrations from physisorbed water and surface hydroxyl groups [25]. The small band at 1610 cm^{-1} (\emptyset) is due to the bending mode of physisorbed water [62]. In the Raman spectrum of the $WO_3-20SiO_2-0.5$ (Fig. 5B), two strong peaks at around 700 cm^{-1} (\ddot{o}) and 800 cm^{-1} (\bullet) correspond to the stretching modes of W–O–W [63]. The positions of these peaks are shifted compared to those in the Raman spectrum of WO_3 -Comm due to the incorporation of these WO_3 domains into the silica matrix. In the range of $200\text{--}400\text{ cm}^{-1}$, the spectrum of WO_3 -Comm displays two separate bands for the bending vibrations of O–W–O bond at 270 cm^{-1} ($*$) and 328 cm^{-1} ($\#$) [63], while the spectrum of $WO_3-20SiO_2-0.5$ exhibits a broad peak in this range that is ascribed to the incorporation of W species in silica [24,34,42,64].

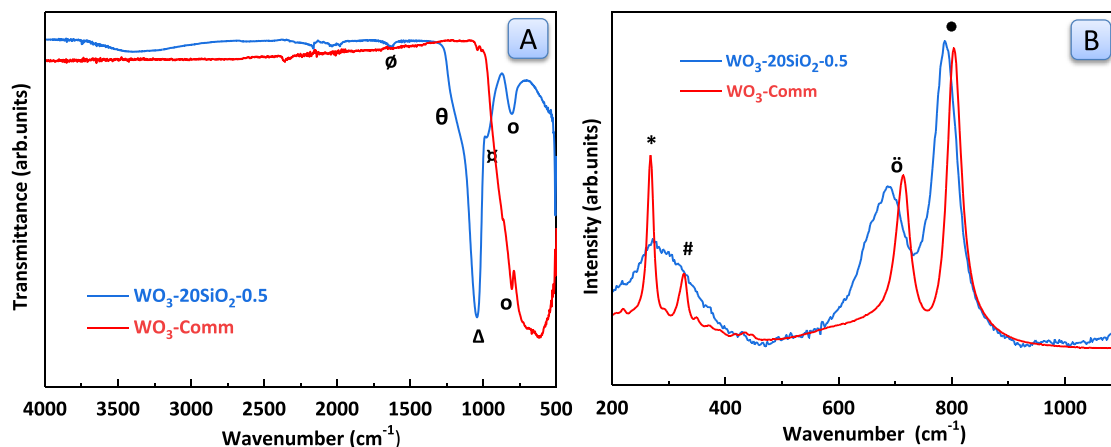


Fig. 5. (A) FT-IR spectra of WO₃-20SiO₂-0.5 and WO₃-Comm. (B) Raman spectra of WO₃-20SiO₂-0.5 and WO₃-Comm.

Next, XPS analysis was conducted in order to shed light on the oxidation state of tungsten (V or VI) and on the chemical composition of WO₃-20SiO₂-0.5. The wide-scan spectrum of WO₃-20SiO₂-0.5 (Fig. S6 and Table S2) shows the expected presence of Si and O as main constituent elements of the sample, together with 2.4 wt% W, in good agreement with the loading obtained by ICP-OES analysis (2.1 wt%). The XPS signals of the W4f and W4d core levels are shown in Fig. 6 and Fig. S7. Although the W4f signal is typically used to study tungsten by XPS [65–67], here the W4d core level was also considered, for the purpose of analyzing the oxidation state of tungsten. As illustrated in the Supporting Information (Fig. S7), two doublets were required in the fitting of the W4f signal. The first one peaked at a binding energy (BE) of 36.9 eV (red in Fig. 6A) and is ascribed to W^{VI}, while the doublet at lower BE (blue in Fig. 6A), i.e. peaking at 35.4 eV, is assigned to W^V [66–69]. Both doublets are shifted towards higher BE with respect to the results reported in previous studies [66–69]. Such a shift has been attributed to tungsten linked by a chemical bond to the SiO₂ matrix [65]. The W4d signal shows two peaks at BEs of 248.3 eV and 261.1 eV (Fig. 6B), which correspond to the spin-orbit split components W4d_{5/2} and W4d_{3/2}, respectively. Their separation is 12.8 eV, suggesting a W^{VI} oxidation state [70]. However, like for the W4f signal, a good fit of the W4d signal requires two doublets

corresponding to the two oxidation states: for the W4d_{5/2} peak the component peaking at 248.7 eV is due to W^{VI} (red in Fig. 6B) and the component at lower binding energy (blue in Fig. 6B), can be assigned to W^V [69,71,72]. Also in this case, the shift of the two doublets towards higher binding energy can be ascribed to the chemical bond between tungsten and the SiO₂ matrix. The XPS signals of the O1s and Si2p core levels did not provide additional information on the W species (see Figs. S8–S10). In summary, the XPS analysis indicates that both W^{VI} and W^V species are present in WO₃-20SiO₂-0.5, and that their relative abundance is similar within the experimental uncertainty (see Table S3).

For W-based epoxidation catalysts, it has been reported that weak Lewis acid sites catalyze the formation of the epoxide product, while Brønsted acid sites promote the formation of the diol [17]. The nature, strength and amount of the acid sites of WO₃-20SiO₂-0.5 was characterized by monitoring the characteristic FT-IR-absorption peaks related to the adsorption of pyridine on Lewis acid sites and on Brønsted acid sites, as a function of temperature (Fig. 7) [63]. The peaks at 1452 cm⁻¹ and 1614 cm⁻¹ are assigned to the characteristic vibration modes of coordinated pyridine on strong Lewis acid sites (which persist upon desorption at 200 °C), while the peaks at 1577 cm⁻¹ and 1596 cm⁻¹ are related to

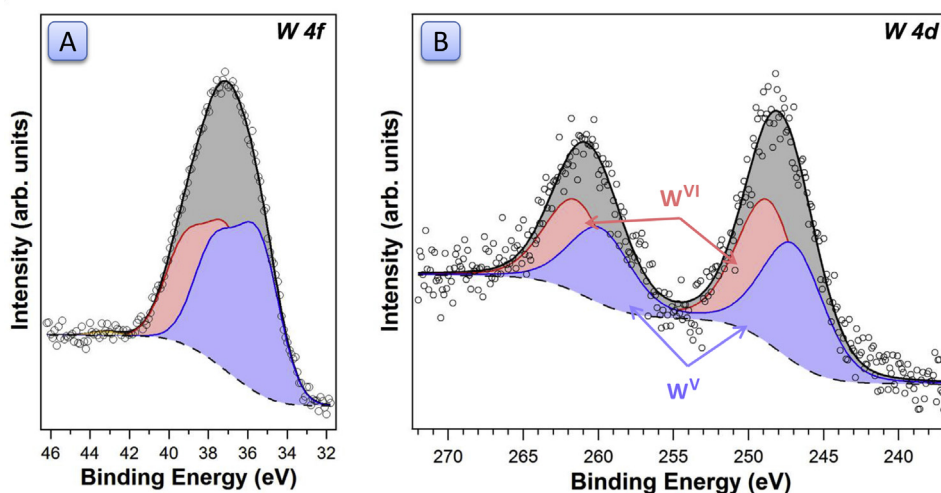


Fig. 6. XPS signals of: (A) W4f and (B) W4d core levels of WO₃-20SiO₂-0.5 and corresponding fits. Two doublet functions were used to deconvolute the W4f signal. The (spin-orbit) splitting energy is (2.2 ± 0.1) eV. The small shoulder at higher binding energy, i.e. 43.2 eV, represents the W 5p_{3/2} core level. In the deconvolution of the W 4d signal, the (spin-orbit) energy splitting is (12.8 ± 0.1) eV.

the vibration modes of coordinated pyridine on weak Lewis acid sites. The peaks at 1540 cm^{-1} are ascribed to the vibration mode of pyridinium ions on Brønsted acid sites [40,42]. Based on the integrated absorbance of Lewis/Brønsted acid bands and molecular absorption coefficients [73], the concentrations of Lewis and Brønsted acid sites were estimated to be 42.3 and 1.3 $\mu\text{mol/g}$, respectively. These results indicate that the $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ catalyst possesses mainly Lewis acid sites, which are the proposed active sites for the epoxidation (Scheme 1), alongside with a small fraction of Brønsted acid sites. These Lewis and Brønsted acid sites can originate from both W^{VI} and W^{V} species coordinated to a silica matrix [74,75]. For each oxidation state, the Lewis acid sites display a higher degree of coordination to Si atoms compared to Brønsted acid sites (Fig. 8). Therefore, the larger fraction of Lewis acid sites observed in our catalyst can be ascribed to the good dispersion of the W sites in the silica matrix that was indicated by XRD, TEM, SEM-EDX and XPS (*vide supra*) and that stems from our scCO_2 -assisted method. This hypothesis is also supported by the fact that the total amount of acids determined by FT-IR of adsorbed pyridine (43.6 $\mu\text{mol/g}$) corresponds to 40% of the W atoms present in $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ (108 $\mu\text{mol/g}$).

Finally, the surface hydrophilicity of the $\text{WO}_3\text{-SiO}_2$ catalysts was evaluated on the basis of their ability to adsorb water molecules as monitored by TGA (see Table 1). It is important to tune the surface hydrophilicity of catalysts for the epoxidation of alkenes with H_2O_2 to ensure a good contact with both apolar alkene and polar H_2O_2 [51]. When comparing the surface hydrophilicity among $\text{WO}_3\text{-SiO}_2$ materials prepared with the same concentration of TMOS solution, those prepared employing lower amounts of basic solution are less hydrophilic. When comparing $\text{WO}_3\text{-SiO}_2$ catalysts synthesized with the same amount of basic solution, those prepared with a higher concentration of TMOS are less hydrophilic. The two most active catalysts identified in this work ($\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ and $\text{WO}_3\text{-}25\text{SiO}_2\text{-}0.5$) are also the two with lowest hydrophilicity.

Based on the above characterization results, the superior catalytic activity of $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ is attributed to a combination of its physicochemical properties: (i) the presence of accessible W species acting as Lewis acid sites; (ii) the high specific surface area ($892\text{ m}^2/\text{g}$) and non-porous, and thus non-confined, open structure of the nanoparticles, which enhance the number and accessibility of catalytic sites; (iii) the relatively low hydrophilicity of its surface, which can facilitate contact with both cyclooctene and H_2O_2 while avoiding strong bonding of water, which may poison the active sites

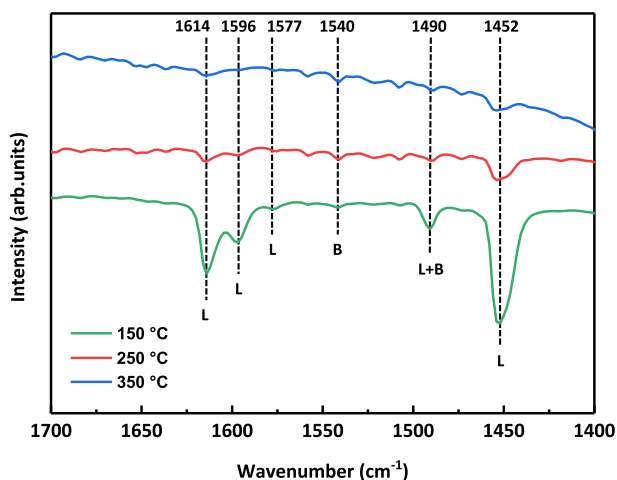


Fig. 7. FT-IR spectra of adsorbed pyridine on the $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ catalyst, recorded at different temperatures.

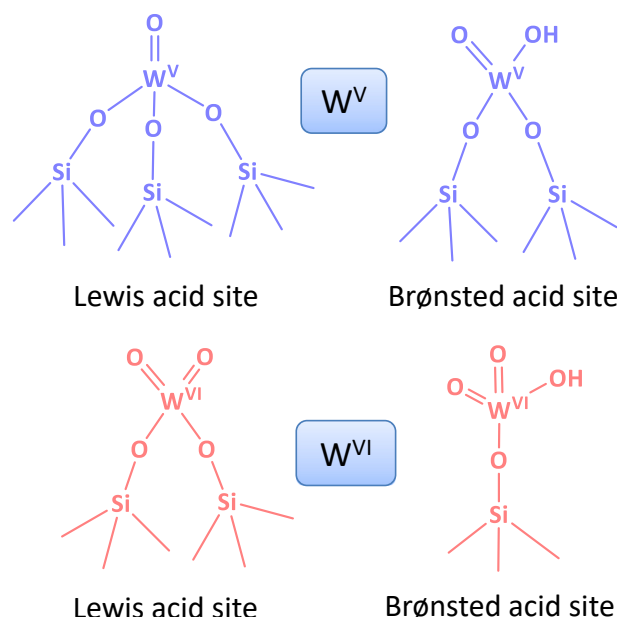


Fig. 8. Proposed models of the structures of W^{V} and W^{VI} species in the $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ catalyst.

[55]; (iv) the good dispersion of W species within the silica matrix, which implies that a large fraction of the W atoms are acting as catalytic sites (the number of accessible Lewis acid sites corresponds to 39% of the total W atoms present in the material) while preventing their leaching and thus granting the observed good reusability of $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$.

3.3. Comparison with other catalysts

The activity of the $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ catalyst prepared with the scCO_2 -assisted sol-gel method was compared with that of a reference catalyst prepared via a similar sol-gel route but without scCO_2 ($\text{WO}_3\text{-SiO}_2\text{-Ref}$) and of bulk WO_3 ($\text{WO}_3\text{-Comm}$). The $\text{WO}_3\text{-SiO}_2\text{-Ref}$ catalyst showed lower cyclooctene conversion (55%) and epoxide yield (55%). It also suffered from leaching of active species (see leaching test result in Fig. S2), which is caused by the existence of large WO_3 particles ($> 50\text{ nm}$) in the material, as proved by TEM-EDX analysis (Fig. S11). On the other hand, these large WO_3 particles are absent in $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$, which also possesses a higher specific surface area ($892\text{ m}^2/\text{g}$) than $\text{WO}_3\text{-SiO}_2\text{-Ref}$ ($826\text{ m}^2/\text{g}$). The structural differences between these two catalysts indicate the importance of employing scCO_2 in the sol-gel synthesis for achieving good dispersion of W species in the silica matrix, high surface area and, consequently, a good catalytic performance in terms of both activity and stability. The second reference catalyst, $\text{WO}_3\text{-Comm}$, displayed a lower but still appreciable cyclooctene conversion (44%) with virtually complete epoxide selectivity, despite the extremely low specific surface area ($3\text{ m}^2/\text{g}$). This is consistent with literature reports that show that bulk WO_3 contains Lewis acid sites that contribute in catalyzing the epoxidation of alkenes [23,29]. The difference in the amount of W between $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ and $\text{WO}_3\text{-Comm}$ was taken into account by calculating and comparing the TON based on W content. The TON number obtained with $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ catalyst is almost two orders of magnitude larger than that for $\text{WO}_3\text{-Comm}$ (328 vs. 5), demonstrating the importance of dispersing the W species in the high surface area $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$.

Further evaluation of the performance of the $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ catalyst can be obtained by comparison with state-of-the-art W-based heterogeneous catalysts for the epoxidation of cyclooctene with H_2O_2 reported in the literature (see Table S4 for an overview). Although the TOF of our optimum catalyst (82 h^{-1}) is lower compared to those of WO_3 nanoparticles (140 h^{-1}) [23] and W-Zn-SnO_2 (147 h^{-1}) [76], the synthesis of $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ is more environmental friendly as it does not require the use of high temperature as in flame spray pyrolysis or Sn as raw material. Additionally, the recovery of $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ is easier compared to the very small WO_3 nanoparticles (average size of 13 nm). A remarkable higher TOF was obtained over $\text{WO}_3\text{-SiO}_2$ (1648 h^{-1}) [43], though only an 8 min reaction was carried out and no leaching test was performed. On the other hand, the TOF of $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ is much higher compared to those of $\text{WO}_3\text{-MCM-}48$ (4 h^{-1}) [28], W-MMM-E (33 h^{-1}) [34] or $\text{W-MCM-}41$ (3 h^{-1}) [35], though these catalysts were tested at lower reaction temperatures, and the leaching of $\text{WO}_3\text{-MCM-}48$ was not addressed while the latter two catalysts suffered from leaching problems. Although a thorough comparison is hindered by the difference in reaction conditions, the catalytic performance of $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ in the epoxidation of cyclooctene with H_2O_2 in terms of conversion, epoxide yield, TON and TOF is also remarkable when compared to state-of-the-art heterogeneous catalysts based on other metal species (e.g. Ti, Ga, Nb) dispersed in a silica matrix (see Table S5).


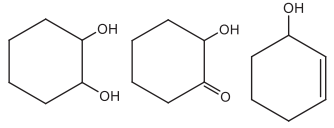
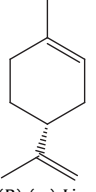
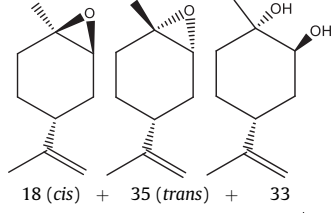
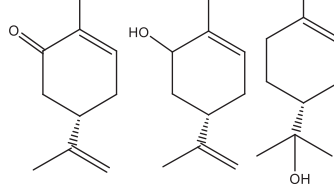
3.4. Substrate scope

Another aspect that we investigated was the versatility of the $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ catalyst, which was explored by expanding the substrate scope to other unsaturated compounds, e.g. cyclohexene and limonene. Cyclohexene oxide is industrially used to prepare cyclohexane diol, an important platform chemical in the synthesis of pharmaceutical products, polyester resins, and liquid crystals

[41,77,78]. The internal oxide of limonene can find application in the synthesis of biodegradable polycarbonate by CO_2 addition [79,80], while the di-oxide of limonene can be employed as a reactive diluent in cationic UV-curing or as a monomer for the production of polyurethanes [55]. Under the optimum reaction conditions (see Table 2), the $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ catalyst was able to convert 84% of cyclohexene, with cyclohexane diol as the main product (78% Sel.) and 2-hydroxy-cyclohexane-1-one (17% Sel., formed by the oxidation of the diol) and 2-cyclohexene-1-ol (5% Sel., formed by the oxidation of the allylic C–H bond of cyclohexene) as side products. No epoxide was observed, in contrast with the high epoxide selectivity observed with cyclooctene (*vide supra*), which stems from the higher stability of cyclooctene oxide [1,81]. The hydrolysis of the epoxide ring leading to the formation of the diol is catalyzed by Brønsted acid sites. $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ displays mainly Lewis acidity (*vide supra*) and has only a relatively small population of Brønsted acid sites. However, the FT-IR spectra of adsorbed pyridine (Fig. 7) show that the intensity of the signal related to Brønsted acid sites does not decrease significantly by increasing temperature, proving the strong nature of these sites. Therefore, the formation of the diol is attributed to the strength rather than to the number of Brønsted acid sites in $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$.

The conversion of limonene over the $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ catalyst reached 54% with a 53% epoxide selectivity under the employed reaction conditions (see Table 2). Among the epoxide products, only the internal epoxide was observed (18% Sel. towards *cis*-internal-oxide; 35% Sel. towards *trans*-internal-oxide), with no terminal epoxide or diepoxide being found. This is ascribed to the electrophilic attack of the oxygen atom from the activated H_2O_2 , which occurs preferentially on the more electron-rich internal C=C bond [82], and to the use of a 1:1 ratio between H_2O_2 and limonene (compared to the 2:1 ratio that would be needed for the theoretical complete conversion of two C=C bonds in limonene). The corresponding diol (33% Sel.) was formed as the main side product,

Table 2
Epoxidation of cyclohexene and (R)-(+)-limonene catalyzed by $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5^a$

Substrate	Conv. (%)	Product Sel. (%)
 Cyclohexene	84	 78 + 17 + 5
 (R)-(+)-Limonene	54	 18 (<i>cis</i>) + 35 (<i>trans</i>) + 33  5 + 3 + 1 + trace amounts of other side products (5)

^a Reaction conditions: 2 mmol substrate, 2 mmol H_2O_2 (50 wt% in aqueous solution), 1 mmol di-*n*-butyl-ether, 250 mg isopropanol, 2.0 g 1,4-dioxane, 40 mg $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ catalyst, 80°C , 4 h.

which is also related to the presence of Brønsted acid sites on the $\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$ catalyst. Minor amounts of three other side products (5% carvone + 3% carveol + 1% terpineol) were also detected. There were a few side products with trace amounts (5% in total) that could not be identified by GC-MS.

4. Conclusions

In this work, $\text{WO}_3\text{-SiO}_2$ with a high specific surface area ($892\text{ m}^2/\text{g}$) and good dispersion of W species was prepared by a novel, template-free supercritical- CO_2 -assisted sol-gel method. For this purpose, a tailored reactor set-up was designed and employed to allow the formation of the $\text{WO}_3\text{-SiO}_2$ materials to take place only in the presence of supercritical CO_2 medium. The method was used to synthesize a series of $\text{WO}_3\text{-SiO}_2$ materials by systematic variation of selected synthetic parameters (TMOS concentration, aqueous ammonia solution, W precursor amount, applying supercritical condition or not). The obtained $\text{WO}_3\text{-SiO}_2$ materials were applied as heterogeneous catalysts for the epoxidation of alkenes with H_2O_2 as oxidant. The most active catalyst was not the material with the highest specific surface area ($1034\text{ m}^2/\text{g}$) but the one combining a high specific surface area ($892\text{ m}^2/\text{g}$) with good dispersion of tungsten species within the silica matrix (as evidenced by XRD, TEM, SEM-EDX and XPS) and relatively low surface hydrophilicity (TGA). The W species display mainly Lewis acid character, thus providing the active sites for the epoxidation, with only a minor fraction of Brønsted acid sites (as shown by FT-IR analysis of adsorbed pyridine). The optimum catalyst ($\text{WO}_3\text{-}20\text{SiO}_2\text{-}0.5$) achieved 73% cyclooctene conversion with > 99% epoxide selectivity at 80°C after 4 h, employing a stoichiometric ratio of H_2O_2 (1:1) in 1,4-dioxane as solvent. Importantly, the common problem associated with the leaching of W species when employing W-based heterogeneous catalysis in the presence of water was prevented by preparing $\text{WO}_3\text{-SiO}_2$ with this synthesis method. This is ascribed to the formation of W–O–Si bond in our material, as proved by FT-IR, Raman, and XPS analysis. The catalyst was reused in five consecutive runs (after washing and thermal treatment) with no loss of activity. Notably, the catalyst is also versatile as it was active in the conversion of cyclohexene to cyclohexane diol and in the transformation of limonene to limonene oxide. Additionally, our novel scCO_2 -assisted sol-gel method has the potential to be extended to the synthesis of other silica-based materials in which metals and silica are homogeneously distributed rather than forming separate domains.

Data availability

All data presented in this work are stored according to the Research Data Management Plan of the University of Groningen and are available upon request.

Author contributions

Yehan Tao: Investigation; Methodology; Formal analysis; Validation; Writing; Visualization.

Oreste De Luca: Investigation; Formal analysis; Writing; Visualization.

Bhawan Singh: Methodology; Resources; Supervision.

Aeilke J. Kamphuis: Methodology; Resources; Supervision.

Juan Chen: Investigation; Formal analysis.

Petra Rudolf: Formal analysis; Supervision; Writing.

Paolo P. Pescarmona: Conceptualization; Methodology; Formal analysis; Supervision; Writing; Visualization; Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mtchem.2020.100373>.

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